

What is claimed is:

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1. A solvent-soluble poly(urethane/urea) resin derived from a polyurethane prepolymer being the reaction product of:

- 5 (a) a diisocyanate component and a diol component having (i) a first diol having a molecular weight below 2000 and (ii) a polymeric diol having a molecular weight below 3000; wherein the -NCO/-OH ratio is less than 2 and containing 1.3 to 6.0 wt. % of unreacted -NCO groups and (b) diamine; wherein the amount of diamine is 80% to 120%, based on the equivalents of unreacted -NCO groups.

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2. The resin of claim 1 wherein the first diol has a lower molecular weight than the polymeric diol

- 15 3. The resin of claim 1 wherein the nitrogen content of the resin derived from the unreacted -NCO groups of the diisocyanate component is from 1.3 to 6.0 wt. % .

4. The resin of claim 1 wherein the polymeric diol comprises 30 to 80 % of the equivalents of the diol component.

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5. The resin of claim 1 wherein the -NCO/-OH ratio is between 1 and 2.

6. The resin of claim 1 having a molecular weight between about 10,000 and about 80,000.

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7. The resin of claim 1 wherein the diisocyanate component comprises two or more diisocyanate compounds.

- 30 8. The resin of claim 1 wherein the diisocyanate component is an aromatic diisocyanate compound, an aliphatic diisocyanate compound, or a mixture thereof.

9. The resin of claim 8 wherein the diisocyanate component is 4,4'-diphenylmethane diisocyanate; 4,4'-dicyclohexyl diisocyanate; hexamethylene diisocyanate; meta-tetramethylene-xylenediisocyanate; isophorone diisocyanate; toluene diisocyanate; or a mixture thereof.

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10. The resin of claim 1 wherein the diisocyanate component comprises isophorone diisocyanate.

10 11. The resin of claim 1 wherein the first diol is selected from the group consisting of aliphatic diols, polyether diols and polycaprolactone diols, and mixtures thereof.

15 12. The resin of claim 11 wherein the first diol is selected from the group consisting of 1,4 butanediol, 1,5 pentanediol, and alpha-hydro-omega-hydroxy-poly(oxy 1,4 butyldiyl) having a molecular weight of 1000.

13. The resin of claim 11 wherein the first diol is an aliphatic diol.

20 14. The resin of claim 11 wherein the aliphatic diol is 1,4-butanediol.

15. The resin of claim 1 wherein the polymeric diol has a molecular weight between 425 and 3000.

25 16. The resin of claim 1 wherein the polymeric diol is a polyether diol or a polycaprolactone diol.

30 17. The resin of claim 1 wherein the polymeric diol is selected from the group consisting of alpha-hydro-omega-hydroxy-poly(oxy-1,4-butyldiyl), and polypropylene glycol.

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AS 18. The resin of claim 17 wherein the polymeric diol is a polycaprolactone.

19. The resin of claim 18 wherein the polycaprolactone has a molecular weight of 2500 or less.

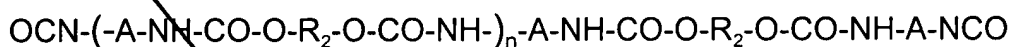
5 20. The resin of claim 1 wherein the diamine is hydrazine, methylene diamine, ethylene diamine, diamino cyclohexane, hexamethylene diamine, piperazine, or isophorone diamine or mixtures thereof.

10 21. The resin of claim 20 wherein the diamine is ethylene diamine, isophorone diamine, or a mixture thereof.

15 22. The resin of claim 1 wherein the organic solvent is an ester or an alcohol/ester mixture.

20 23. The resin of claim 22 wherein the ester is ethyl acetate or n-propyl acetate; and the alcohol is methanol, ethanol, n-propanol, isopropanol, or butanol.

25 24. The resin of claim 1 wherein the polyurethane prepolymer has the structure:



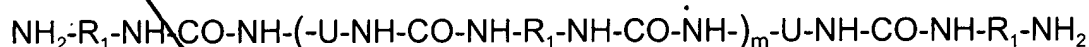
wherein -A- is an aryl or alkyl group; and R_2 comprises R_3 and R_4 ; wherein R_3 is an alkyl or a polymeric group having a molecular weight below 2000; wherein R_4 is a polymeric group having a molecular weight below 3000.

25 25. The resin of claim 24 wherein the molecular weight of R_3 is less than the molecular weight of R_4 .

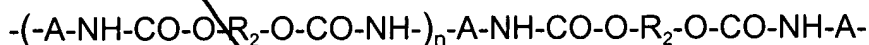
30 26. The resin of claim 24 wherein R_2 comprises from about 30 to about 80 equivalent % of R_4 .

27. The resin of claim 24 wherein the ratio of R_4 to R_3 ranges between about 90:10 and about 10:90.

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SubCS 28. The resin of claim 1 wherein the poly(urethane/urea) resin has the structures



10 wherein R_1 is a covalent bond or a C_{1-10} alkyl group and -U- has the structure:



15 wherein -A- is an aryl or alkyl group; and R_2 comprises R_3 and R_4 , wherein R_3 is an alkyl or a polymeric group having a molecular weight below 2000, and wherein R_4 is a polymeric group having a molecular weight below 3000.

Sub A1 29. A solvent-based flexographic and gravure compatible laminating printing ink comprising:

20 (A) a solvent-soluble poly(urethane/urea) resin which is derived from a polyurethane prepolymer being the reaction product of:

(a) a diisocyanate component and a diol component having: (i) a first diol having a molecular weight below 2000 and (ii) a polymeric diol having a molecular weight below 3000; wherein the -NCO/-OH ratio is less than 2 and containing 1.3
25 to 6.0 % by weight of unreacted -NCO groups and (b) diamine; wherein the amount of diamine is 80% to 120% based on the equivalents of unreacted -NCO groups;
(B) a colorant; and
(C) an organic solvent.

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30. The ink of claim 29 wherein the colorant is a pigment, dye or a mixture

thereof.

31. The ink of claim 29 wherein the organic solvent is an ester or an alcohol/ester mixture.

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32. The ink of claim 31 wherein the ester is ethyl acetate or n-propyl acetate; and the alcohol is methanol, ethanol, n-propanol, isopropanol, or butanol.

33. The ink of claim 29 further comprising a polymeric dispersant.

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34. The ink of claim 33 wherein the polymeric dispersant is a nitrocellulose

35. The ink of claim 33 wherein the polymeric dispersant is a polyvinyl butyral.

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36. The gravure compatible laminating printing ink of claim 29 comprising:
about 8 to about 60 % solvent-soluble poly(urethane/urea) resin;
about 3 to about 30 % colorant; and
about 15 to about 60 % organic solvent.

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37. The flexographic compatible laminating printing ink of claim 29 comprising:

about 8 to about 60 wt. % solvent-soluble poly(urethane/urea) resin;

about 3 to about 30 wt. % colorant; and

25 about 15 to about 60 wt. % organic solvent.

38. The ink of claim 29 further comprising an ink viscosity between 15 and 30 seconds as measured using a # 2 efflux cup.

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39. A method for printing on a polymeric substrate comprising the steps:
applying the laminating ink of Claim 29 onto the surface of the polymeric substrate

to form an image; and drying the image to form a polymeric substrate having a tack-free, firmly adherent laminating ink which is un-blocked when contacted under pressure at ambient temperatures with a second surface of the substrate.

5 40. The method of claim 39 wherein the ink is applied to the polymeric substrate with a flexographic printing press.

 41. The method of claim 39 wherein the ink is applied to the polymeric substrate with a gravure printing press.

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 42. The method of claim 39 further comprising applying a second substrate surface to the image to form a laminate.

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 43. The method of claim 42 wherein the second substrate surface is formed by melt extrusion.

 44. The method of claim 42 wherein the second substrate surface has an adhesive surface.

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 45. The method of claim 42 further comprising subjecting the laminate to retort conditions, thereby forming a retorted laminate wherein the image remains substantially unchanged and is free of delamination defects.

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 46. The method of claim 39 wherein the polymeric substrate is polyethylene, polypropylene, polyethylene terephthalate, cellulose acetate, cellulose acetate butyrate, polycarbonate, polyamide, polyvinylidenechloride coated polyethylene terephthalate, polyvinylidenechloride coated polypropylene, metallized polyethylene terephthalate, and metallized polypropylene.

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 47. The method of claim 39 wherein the polymeric substrate is a polypropylene or a polyester film or sheet.

48. The method of claim 42 wherein the second substrate is a polymeric substrate.

5 49. The method of claim 42 wherein the second substrate is a polyethylene.

10 50. An improved method of producing a poly(urethane/urea) resin involving the steps of: (a) preparing a polyurethane prepolymer solution by reacting a diisocyanate component, a diol component, and a condensation polymerization catalyst in an organic solvent, wherein the resulting polyurethane prepolymer contains unreacted -NCO groups; and (b) reacting the polyurethane prepolymer with a diamine; wherein the improvement comprises: (c) preparing the diamine a solvent mixture comprising an alcohol and a second organic solvent; and (d) adding at a controlled rate the polyurethane prepolymer solution to the diamine solution.

15 51. The method of claim 50 wherein the solvent mixture contains between about 10 to about 75 wt. % of the alcohol.

20 52. The method of claim 50 wherein the organic solvent and the solvent mixture are identical.

25 53. The method of claim 50 wherein the organic solvent and the second organic solvent are identical.

54. The method of claim 50 wherein the polyurethane prepolymer solution is added such solution at a controlled rate by titrating it into the diamine solution.